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## Effect of exposure conditions and concrete quality on pyrrhotite oxidation and internal sulfate attack

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### Abstract

Thousands of homes in County Donegal, Ireland, are damaged by cracks formed a few years after construction. The authorities have erroneously attributed the damages to the presence of muscovite mica in the concrete blocks used to build the homes. Only recently, research has shown that pyrrhotite oxidation triggering internal sulfate attack (ISA) is the cause. In this study, the strip foundation, the rising blocks elevating the structure to ground level and the inner and outer leaf of one affected home are investigated. As these four types of structural components differ by concrete quality, exposure condition or both, their effect on pyrrhotite oxidation and ISA is investigated. Sulfur analysis, X-ray diffraction and scanning electron microscopy are used to characterize the concrete.

**Keywords:** concrete, ettringite, internal sulfate attack, pyrrhotite, thaumasite

## 1. INTRODUCTION

Concrete blocks with micaceous phyllite containing pyrrhotite as aggregate have been used to build homes in Ireland since approximately 20 years, with a culmination during a building boom between 2000 and 2008. The homes are typically built with strip foundations of poured concrete as a first step. Rising blocks turned sideways are stacked up to reach the ground level. There, the outer leaf and the load-carrying inner leaf, separated by a layer of insulation and connected with stainless steel wall ties, are placed on the rising blocks using concrete blocks put upright. In county Donegal, thousands of homes have developed cracks after a few years, mainly in the outer leaf and to a lesser extent in the inner leaf. Affected outer leaves show clear signs of concrete expansion with vertical and horizontal cracks. The expansion pushes the concrete blocks towards the corners of the homes where the corner blocks often fall off. In some cases outer leaves bulging outwards or twisting chimneys can be observed. The authorities have attributed the extensive damages to the presence of mica [1]. However, recent research has demonstrated that oxidizing pyrrhotite present in the phyllite aggregate provokes internal sulfate attack (ISA) and causes the widespread damages [2]. Comparable problems affecting concrete foundation of homes have been reported from North America [3-5].

In a project financed by the Department of Housing, local Government and Heritage and Geological Survey of Ireland, a consortium is investigating four homes located in County Donegal, in northwest Ireland. This study reports the results obtained so far from one of the investigated homes. The four different structural components (inner and outer leaf, rising blocks, strip foundation) have been investigated to assess the influence of exposure conditions and concrete quality on pyrrhotite oxidation and ISA. Sulfur analysis, X-ray diffraction and scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) have been used to characterize the concrete.

## 2. MATERIALS AND METHODS

The investigated home displays some minor cracking on the inner leaf and extensive cracking on the outer leaf. In order to take samples from the rising blocks and the strip foundation, the structural

components had to be excavated down to over 2 meters below ground level using a digger. The core from the rising wall was taken about 40 cm above the strip foundation.

Two entire blocks, one from the inner leaf, the other one from the outer leaf, with approximate dimensions of  $10 \times 25 \times 48 \text{ cm}^3$  were available for analysis. Two cores with diameter of 100 mm and length of  $\sim 32$  and  $\sim 20$  cm, respectively, were obtained from the rising blocks and the strip foundation.

One core with diameter of 80 mm and length of 80 mm was taken for the compressive strength test from each block. Freshly cut surfaces were used for the phenolphthalein test. About 500 g of concrete was crushed to a size  $< 1 \text{ mm}$  for sulfur analysis. The fraction  $< 125 \mu\text{m}$  was separated by sieving and carefully ground to a size  $< 63 \mu\text{m}$  for XRD using in an agate mortar. The samples for the microstructural analysis were cut, oven dried at  $50 \text{ }^\circ\text{C}$  for three days, impregnated with an epoxy containing fluorescent dye, polished and carbon coated.

Compressive strength was determined after 28 days according to EN 12390-3:2019. The analysis of sulfur present as sulfide was conducted according to EN 196-2:2013. XRD was measured using a PANalytical X'Pert Pro MPD diffractometer in a  $\Theta$ - $\Theta$  configuration with  $\text{CoK}\alpha$  radiation, a fixed divergence slit size of  $0.5^\circ$ , a rotating sample stage and the X'Celerator detector. The microstructural analysis of the samples was performed with a SEM FEI Quanta 650 using a pressure between 3.0 and  $4.0 \times 10^{-6}$  Torr. Elemental analysis were conducted by EDS with a Thermo Noran Ultra Dry 60mm<sup>2</sup> detector and Pathfinder X-Ray Microanalysis Software. An acceleration voltage of 12 kV and a spot size of 4.5 were used for imaging, EDS point analysis. Acceleration voltage and spot size were increased for the elemental maps to 20 kV and 5, respectively. Concentrations are given in atom-%. The phase clustering to determine the mica content was performed according to [6].

### 3. RESULTS

The results are summarized in Table 1.

The compressive strength is in a typical range for the concrete blocks [2], 11.6 MPa and 6.7 MPa for the inner and outer leaf, respectively (Table 1).

The phenolphthalein test shows that both the inner and the outer leaf are carbonated, while the rising blocks and the foundation turn pink and consequently are not carbonated (Table 1).

Sulfur present as sulfide ranges from 0.49 to 0.75 mass-% of the concrete (Table 1) and is considerably higher than the limit value of 0.1 mass-% given by EN 12620:2008 for aggregates containing pyrrhotite.

XRD shows the same minerals present in the concrete aggregates of all concrete blocks with chlorite, muscovite, quartz, albite, calcite and rutile (Table 1). The inner and outer leaf are devoid of portlandite, confirming the results of the phenolphthalein test. Ettringite is present in the rising blocks and the outer leaf, showing that carbonation is not complete in the outer leaf. Although ettringite is not present in the inner leaf, thaumasite is detected in addition to gypsum. These two secondary sulfate phases are present as well in the outer leaf.

Phyllite is identified by SEM and EDX as the main aggregate, with schist as a secondary lithology. In addition to the minerals already detected by XRD, the iron sulfides pyrrhotite and pyrite can be identified. Pyrrhotite is considerably more abundant than pyrite. The mica content (sum of muscovite and chlorite) ranges between 19-26 volume-% (Table 1).

The hydrates typical for Portland cement (calcium-silicate-hydrate (C-S-H), portlandite, ettringite, monocarbonate) are present in the foundation concrete (Fig. 2A). However, there are two peculiarities. First, C-S-H displays a higher Si/Ca-ratio than usual, with a value of  $\sim 0.70$  instead of  $\sim 0.54$  (not shown). Secondly, there is an unusual high amount of monocarbonate present (Fig. 2A). Pyrrhotite particles show some minor oxidation, with an occasionally increased amount of sulfur in the adjacent cement paste. However, the released amount of sulfur is too low to already show an impact on the hydrates in the bulk cement paste.

The main difference in the hydrate assemblage in the rising block compared to the foundation is the clear shift from C-S-H towards ettringite (Fig. 2B). Monocarbonate is still present.

The shift towards ettringite is even more pronounced in the outer leaf (Fig. 2C). Additionally, there is an intermixture of thaumasite and gypsum with a minor amount of ettringite. C-S-H is strongly decalcified, portlandite and monocarbonate are absent and calcite and Si-Al-gel have formed instead (not shown).

In the fully carbonated inner leaf, the cement hydrates have been completely altered (Fig. 2D). Calcite and Si-Al-gel, often with an unusually high Mg content, dominate (not shown). There are some traces of thaumasite left and gypsum occurs as the main secondary sulfate phase.

Table 1: Summary of the results. Relative amount of the different components with  $XX > X > x$ .

Component	Inner leaf	Outer leaf	Rising blocks	Foundation
compressive strength [MPa]	11.6	6.7	n.a.	n.a.
bulk density [kg/m <sup>3</sup> ]	2217	1962	n.a.	n.a.
phenolphthalein test	carbonated	carbonated	uncarb.	uncarb.
S as sulfide [mass-%]	0.66	0.49	0.65	0.75
XRD				
<i>monocarbonate</i> <sup>1</sup>	x	-	XX	n.a.
<i>portlandite</i> <sup>1</sup>	-	-	X	n.a.
<i>ettringite</i> <sup>1</sup>	-	x	x	n.a.
<i>thaumasite</i> <sup>1</sup>	X	x	-	n.a.
<i>gypsum</i> <sup>1</sup>	XX	X	-	n.a.
<i>calcite</i> <sup>1,2</sup>	x	x	x	n.a.
<i>chlorite</i> <sup>2</sup>	XX	XX	XX	n.a.
<i>muscovite</i> <sup>2</sup>	XX	XX	XX	n.a.
<i>quartz</i> <sup>2</sup>	X	X	X	n.a.
<i>albite</i> <sup>2</sup>	x	x	x	n.a.
<i>calcite</i> <sup>1,2</sup>	x	x	x	n.a.
<i>rutile</i> <sup>2</sup>	x	x	x	n.a.
microscopy				
C-S-H <sup>1</sup>	x	x	X	X
<i>monocarbonate</i> <sup>1</sup>	-	-	X	XX
<i>portlandite</i> <sup>1</sup>	-	-	x	x
<i>ettringite</i> <sup>1</sup>	x	XX	XX	x
<i>thaumasite</i> <sup>1</sup>	x	x	-	-
<i>gypsum</i> <sup>1</sup>	X	x	-	-
Si-Al-gel <sup>1</sup>	X	x	x	-
CaCO <sub>3</sub> <sup>1</sup>	X	x	-	-
<i>mica (muscovite + chlorite) content [volume-%]</i>	19	26	26	19

<sup>1</sup>components of the cement paste, <sup>2</sup>components of the aggregates

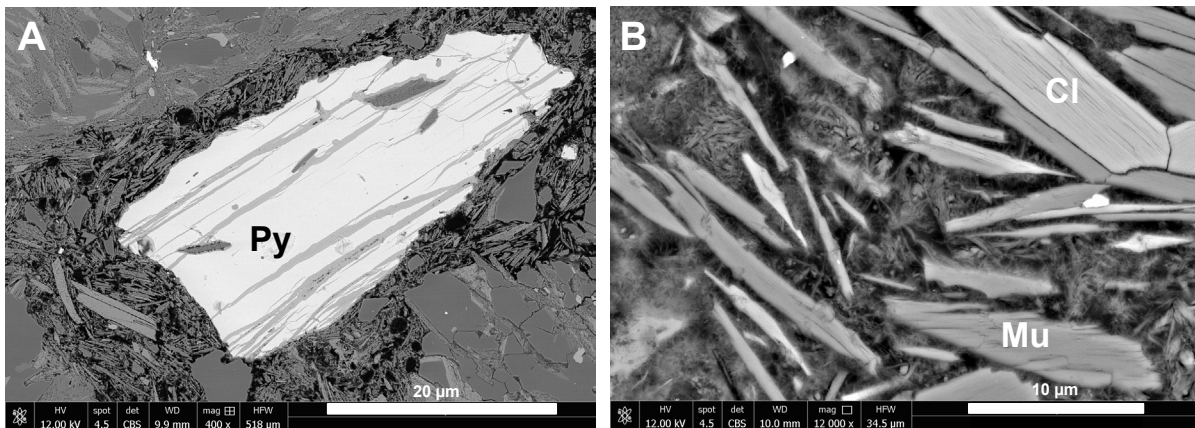


Fig. 1: Pyrrhotite (bright grey; Py) with oxidized layers (medium grey) in the concrete of the inner leaf (A). Muscovite (Mu) and chlorite (Cl, slightly higher back-scattering contrast than muscovite) embedded in a mixture of C-S-H and ettringite in the concrete of the outer leaf.

## 4. DISCUSSION

Pyrrhotite oxidation with ISA can be clearly identified as the process leading to the observed damages in the investigated home. The formation of iron oxides and hydroxides leads to a first volume increase [2,7]. The released sulfuric acid is buffered by the hydroxide ions in the cement paste, where the sulfur

reacts with monocarbonate to form ettringite, causing a pronounced volume increase [2]. When all monocarbonate has reacted, thaumasite will form, followed by gypsum in the case of carbonated concrete as explained in detail in [2]. Thaumasite formation leads to a considerable strength loss of the concrete.

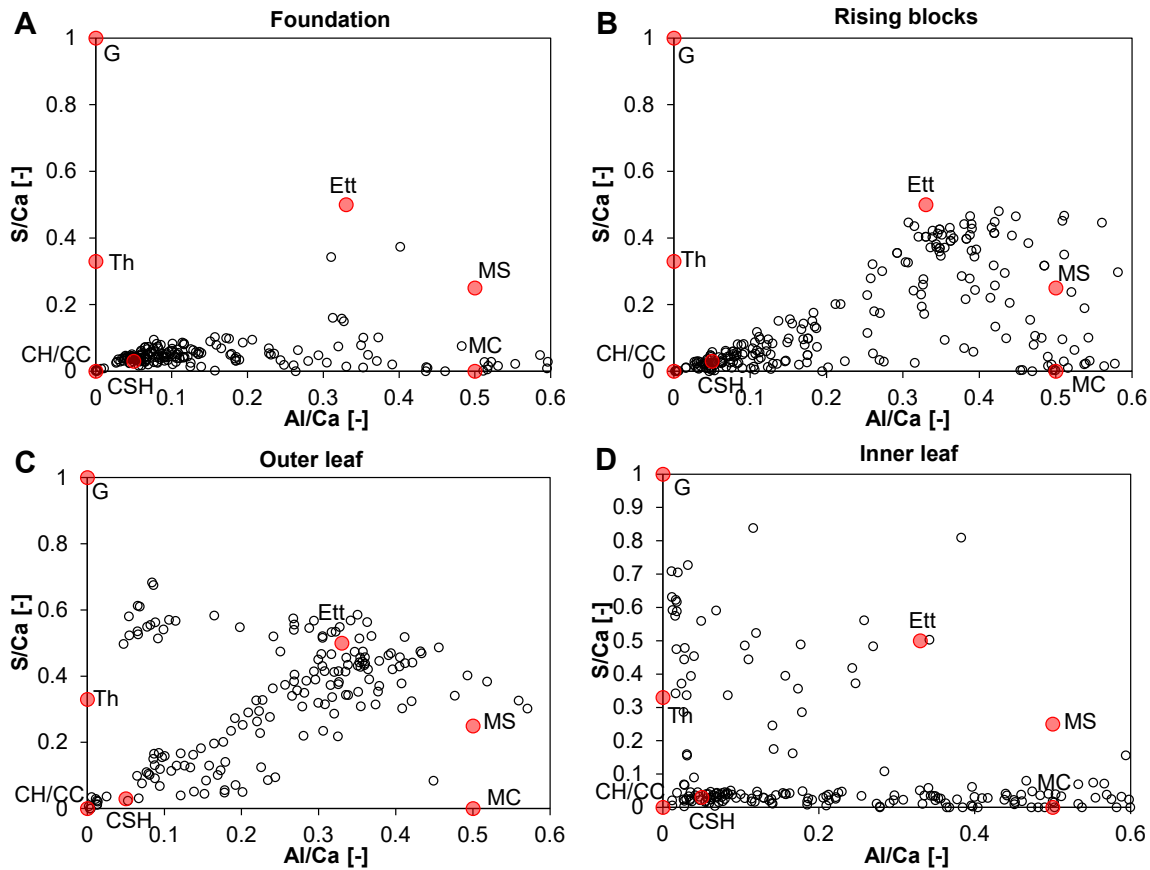


Fig. 2: S/Ca-ratio as a function of Al/Ca-ratio in the concrete of different structural components. The shift from C-S-H to monocarbonate in the inner leaf is not caused by the presence of monocarbonate but by the decalcification of C-S-H due to carbonation. The abbreviations indicate the following pure phases: CH/CC = portlandite/calcite, CSH = C-S-H, Ett = ettringite, G = gypsum, MC = monocarbonate, MS = monosulfate, Th = thaumasite, G = gypsum.

The exposure conditions in the four different structural components influence ISA. As carbonation proceeds faster at relatively dry conditions than at high relative humidity [8,9], the inner leaf with no exposure to the weather is fully carbonated, while the outer leaf protected by a render from direct rain is not fully carbonated, with ettringite and thaumasite still present. On the other hand, pyrrhotite oxidation proceeds faster at higher relative humidity [10]. Therefore, the potential for pyrrhotite oxidation and ISA is larger in the outer leaf compared to the inner leaf, agreeing with the more pronounced damages in the outer leaf. Moreover, the slower progress of carbonation in the outer leaf provides a longer time window for ettringite-induced expansion, a more expansive reaction than the formation of gypsum in carbonated concrete [2]. Consequently, the potential for expansion in the inner leaf is decreased after its carbonation. As such, the secondary minerals formed in the inner and outer leaf are in agreement with ISA in County Mayo (Ireland) [11]. However, the culprit in County Mayo is framboidale pyrite.

The environmental boundary conditions in the rising blocks and the foundation are completely different to the ones in the inner and outer leaf. As these structural components are buried below ground, it can be expected that their level of water saturation is very high. In these conditions, gas diffusion is limited [12]. Consequently, carbonation and pyrrhotite oxidation are slowed down. Additionally, an increased concrete quality, at least for the strip foundation, decreases oxygen diffusion [13] and its availability for oxidation processes. The lower amount of ettringite formed in the rising blocks compared to the outer leaf and the so far only marginal pyrrhotite oxidation in the foundation confirm these considerations. However, it has to be emphasized that pyrrhotite oxidation with ISA is only slowed down by the specific

exposure conditions and the higher concrete quality. The potential for a deleterious reaction and expansion in the future persists.

The low Si/Ca-ratio of the C-S-H and the high monocarbonate content in the foundation and the relatively high Mg content of the Si-Al-gel in the inner leaf clearly point towards an internal source of Si, Al and Mg in the concrete. This is a clear indication that muscovite and chlorite are not stable in the alkaline environment of the concrete and are partly dissolved, leading to an additional formation of C-S-H and monocarbonate. As such, they contribute to concrete strength and may partly compensate the decrease of concrete quality due to their high surface area and high water demand during concrete production [14].

## 5. SUMMARY AND CONCLUSIONS

The investigated home is affected by pyrrhotite oxidation with ISA. Exposure conditions and concrete quality influence the kinetics of the reaction and with it the degree of damage in the different structural components of the home. While the relatively low concrete quality in the outer leaf and the high availability of moisture favour a fast pyrrhotite oxidation and the formation of ettringite and thaumasite, the impact of ISA is reduced in the inner leaf due to the faster carbonation as a result of the lower moisture content in the concrete. The high water saturation in rising blocks and the foundation slows down gas diffusion. As a result, both carbonation and pyrrhotite oxidation proceed very slowly. While there is only minor pyrrhotite oxidation so far in the foundation made with a relatively high quality concrete, the rising blocks show an ongoing ISA with secondary ettringite formation. The expansion of the rising blocks can be expected to push the inner and outer leaf upwards, likely causing cracking. The ISA in the rising blocks will proceed in the future and the potential for ISA and expansion in the foundation remains high over the coming decades.

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